Suppression of Recrystallization of Isotactic Polystyrene Single Crystals by Chemical Modification

Introduction

The occurrence of multiple peaks during scanning crystalline polymers in a differential scanning calorimeter has been the subject of several papers.

In the case of bulk-crystallized polymers, some papers suggested that multiple melting peaks were caused by the presence of morphologically different crystal structures.[1,2] However, more recent investigations have shown that multiple melting originates from melting and recrystallization during the scanning.[3–5] In the case of polymer single crystals, Bair et al.[6] have shown that multiple melting of polyethylene single crystals is inhibited by γ-irradiation.

In our previous paper concerning the melting behavior of isotactic polystyrene (i-PS) we concluded that recrystallization can take place in both bulk- and solution-crystallized i-PS and thus give rise to two melting peaks.[7] In this note we give more evidence for this conclusion based on the melting behavior of chemically modified single crystals of i-PS.

Experimental

Our i-PS is the same sample we used previously.[7] The contaminating 10% atactic polystyrene (a-PS) was removed by dissolving the material in methylene chloride (1 g/100 ml) and dropping the solution into 1 liter of boiling methyl ethyl ketone. After evaporation of methylene chloride, the i-PS precipitated quantitatively from the ketone at room temperature, leaving a-PS in solution. Thus highly stereoregular i-PS was obtained with $\bar{M}_n = 185{,}000$ and $\bar{M}_v = 330{,}000$.

The i-PS single crystals were grown from dilute solutions in dioctylphthalate at 125°C. These crystals were chemically modified by a Friedel-Craft acylation. To 100 ml of nitrobenzene at 50°C we added 0.5 g of i-PS single crystals, about 0.25 g $AlCl_3$, and 1 ml of benzoyl chloride. The $AlCl_3$ dissolved in nitrobenzene, but the single crystals did not, since the reaction temperature of 50°C is far below their dissolution temperature of about 100°C. After 2 hr we poured the reaction mixture into a mixture of methanol/HCl (0.1N). After filtration the collected crystals were washed thoroughly with methanol and ether and dried under vacuum at 50°C. Microanalysis of these acylated crystals yielded: C, 90.75%; H, 7.12 %; O, 1.88 %.

Both the original and the acylated single crystals were further characterized. Figure 1 shows their infrared spectra obtained with a Perkin-Elmer infrared spectrometer type 457, Figure 2 their x-ray spectra obtained with a Philips diffractometer, and Figure 3 their melting curves on a Perkin-Elmer differential scanning calorimeter 1B.

Results and Discussion

The Friedel-Crafts reaction is known to introduce benzoyl groups on the phenyl groups of polystyrene. By using a reaction medium which easily dissolves $AlCl_3$ as well as amorphous i-PS but does not dissolve the i-PS single crystals, we expected that a considerable proportion of the phenyl groups in the amorphous surface layers of the crystals had reacted. Indeed, Figure 1 clearly shows that benzoylation yields an extra infrared absorption band at 1660 cm^{-1} which is characteristic for diaryl ketones. Moreover, the x-ray spectra in Figure 2 demonstrate that the crystalline structure of the single crystals remained intact during the acylation.

From the microanalysis data one can calculate that approximately 25% of all phenyl groups of the single crystals had reacted. Applying the method proposed by Challa et al.[8] to the x-ray spectrum (*b* in Fig. 2) results in an estimate of 40% crystallinity. So,

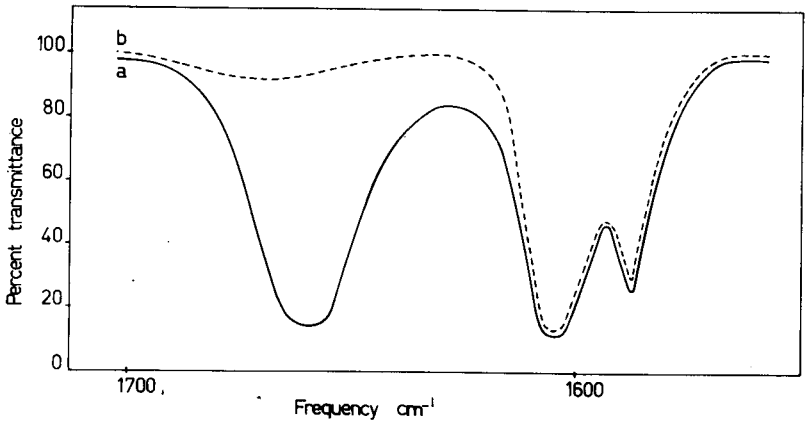

Fig. 1. Infrared spectra of isotactic polystyrene single crystals: (*a*) benzoylated; (*b*) unmodified

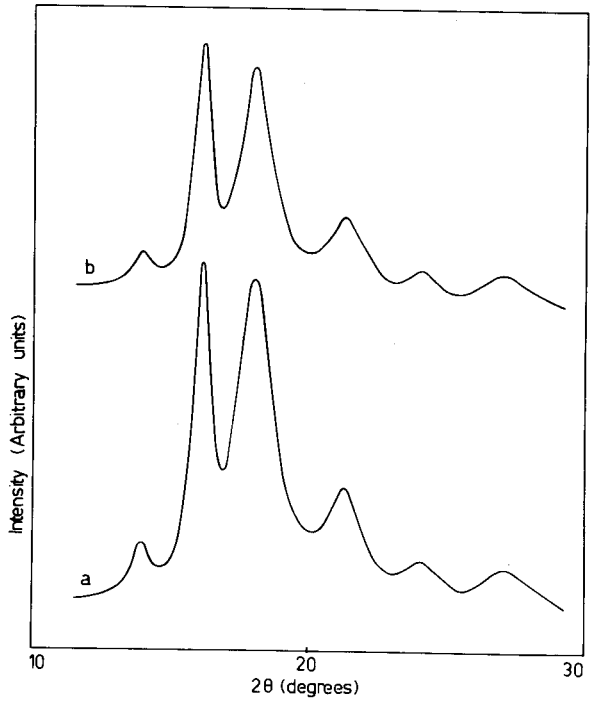

Fig. 2. X-Ray diffractometer scans of isotactic polystyrene single crystals: (*a*) benzoylated; (*b*) unmodified

we may conclude that roughly 40% of the phenyl groups in the amorphous regions had reacted.

The DSC traces in Figure 3 show that the chemically modified crystals give just one melting peak upon scanning, whereas two peaks appear during scanning of the normal crystals. In the latter case, the lower melting peak is the "real" melting peak of the

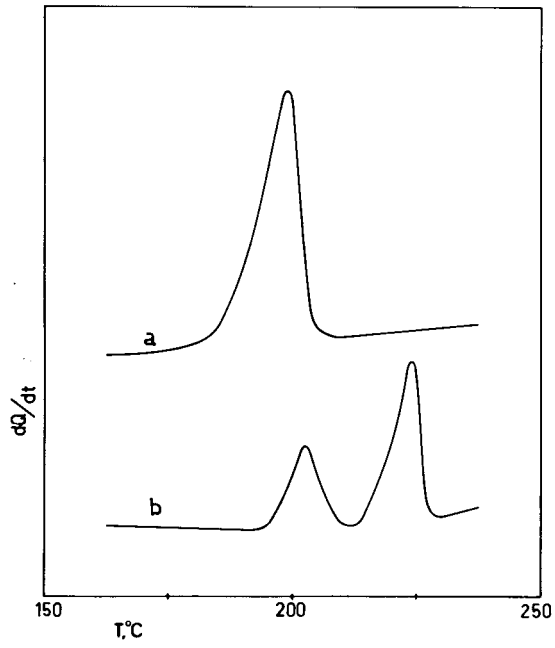

Fig. 3. DSC melting curves of isotactic polystyrene single crystals (heating rate 16°C/min): (*a*) benzoylated; (*b*) unmodified. The ordinate is in arbitrary units.

crystals, and the higher one originates from recrystallization during the scan. This recrystallization process is continuous, and the temperature of the resulting high melting peak depends only on the heating rate in the DSC.[7] The exact mechanism of the recrystallization is not yet clear in the case of i-PS, but we assume that melting of the primary crystalline structure enables the polymer chains to rearrange into more perfect crystals upon further heating. This view is supported now by the absence of a higher melting peak in the case of modified crystals. These crystals have large benzoyl substituents on many phenyl groups in the amorphous layers and are, therefore, not capable of reorganizing to more perfect higher melting crystals during scanning.

The peak temperature of the modified crystals is some degrees lower than the lower melting peak temperature of unmodified crystals. This can be explained by considering the DSC recording of the unmodified crystals as a net heat effect of melting (endotherm) and recrystallization (exotherm). So, during melting recrystallization starts and the maximum in the recorded melting curve shifts to a somewhat higher temperature than the peak temperature of a melting endotherm without recrystallization.

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P. J. Lemstra
A. J. Schouten
G. Challa

Laboratory of Polymer Chemistry
State University Groningen
the Netherlands

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